

AD-A199 656

## OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0659

Technical Report No. 11

**<sup>15</sup>N CP/MAS NMR OF ARAMIDS: A NEW TOOL  
FOR CHARACTERIZATION OF THE MORPHOLOGY OF  
HIGH MODULUS FIBERS FOR COMPOSITES**

by

*Lon J. Mathias and Douglas G. Powell*

Submitted to

Journal of the American Chemical Society

Department of Polymer Science  
University of Southern Mississippi  
Southern Station Box 10076  
Hattiesburg, MS 39406-0076

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

DTIC  
ELECTE  
JUL 20 1988  
S H D

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION NONE		1b. RESTRICTIVE MARKINGS NONE									
2a. SECURITY CLASSIFICATION AUTHORITY NONE		3. DISTRIBUTION/AVAILABILITY OF REPORT UNLIMITED									
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE NONE											
4. PERFORMING ORGANIZATION REPORT NUMBER(S)  Technical Report No. 11		5. MONITORING ORGANIZATION REPORT NUMBER(S)  ONR N00014-86-K-0659									
6a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION  Office of Naval Research									
6c. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Polymer Science Department Southern Station Box 10076 Hattiesburg, MS 39406-0076		7b. ADDRESS (City, State, and ZIP Code)  800 North Quincy Avenue Arlington, VA 22217									
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER									
8c. ADDRESS (City, State, and ZIP Code)  800 N. Quincy Avenue Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS <table border="1"><tr><td>PROGRAM ELEMENT NO.</td><td>PROJECT NO.</td><td>TASK NO.</td><td>WORK UNIT ACCESSION</td></tr><tr><td></td><td></td><td></td><td></td></tr></table>		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION				
PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION								
11. TITLE (Include Security Classification) <sup>15</sup> N CP/MAS NMR of Aramids: A New Tool for Characterization of the Morphology of High Modulus Fibers for Composites											
12. PERSONAL AUTHOR(S) Lon J. Mathias and Douglas G. Powell											
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 8/87 TO 7/88	14. DATE OF REPORT (Year, Month, Day) 1988/July/15	15. PAGE COUNT								
16. SUPPLEMENTARY NOTATION  Journal of the American Chemical Society											
17. COSATI CODES <table border="1"><tr><th>FIELD</th><th>GROUP</th><th>SUB-GROUP</th></tr><tr><td></td><td></td><td></td></tr></table>		FIELD	GROUP	SUB-GROUP				18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)			
FIELD	GROUP	SUB-GROUP									
<p>Natural abundance <sup>15</sup>N solid state NMR was found to provide unique molecular and microscopic level information on aramids and aramid-containing copolymers. Poly(p-phenyleneterephthalamide) (PPTA) coagulated from H<sub>2</sub>SO<sub>4</sub> into water displayed a broad envelope of overlapping peaks between 90 and 100 ppm (relative to solid glycine). Annealing significantly reduced the width of this envelope although not to the level of the commercial Kevlar fiber spectrum. Molecular level composites of PPTA grafted with nylon 3 in a nylon 3 matrix showed broad peaks for the aramid components up to 30% by weight content. Peak widths were comparable to that of the precipitated PPTA. Above 30% PPTA, phase separation (confirmed by IR, x-ray and SEM) is observed by solid state NMR as narrower peaks for the aramid nitrogens. Poly(p-benzamide) (PBA) powder shows similar behavior to PPTA before and after annealing. A block copolymer of PBA with nylon 6 (80% PBA) showed a much sharper peak for the aramid nitrogens consistent with a greater degree of uniformity and order in this material. While detailed assignment of all peaks observed is not complete, the value of the method for characterizing aramid-containing materials was clearly demonstrated.</p>											
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION									
22a. NAME OF RESPONSIBLE INDIVIDUAL Lon J. Mathias		22b. TELEPHONE (Include Area Code) (601)266-4868	22c. OFFICE SYMBOL								

**<sup>15</sup>N CP/MAS NMR of Aramids: A New Tool for Characterization  
of the Morphology of High Modulus Fibers for Composites**

Douglas G. Powell and Lon J. Mathias\*  
Department of Polymer Science  
University of Southern Mississippi  
Hattiesburg, Mississippi 39406-0076

**ABSTRACT**

Natural abundance <sup>15</sup>N solid state NMR was found to provide unique molecular and microscopic level information on aramids and aramid-containing copolymers. Poly(p-phenyleneterephthalamide) (PPTA) coagulated from H<sub>2</sub>SO<sub>4</sub> into water displayed a broad envelope of overlapping peaks between 90 and 100 ppm (relative to solid glycine). Annealing significantly reduced the width of this envelope although not to the level of the commercial Kevlar fiber spectrum. Molecular level composites of PPTA grafted with nylon 3 in a nylon 3 matrix showed broad peaks for the aramid components up to 30% by weight content. Peak widths were comparable to that of the precipitated PPTA. Above 30% PPTA, phase separation (confirmed by IR, x-ray and SEM) is observed by solid state NMR as narrower peaks for the aramid nitrogens. Poly(p-benzamide) (PBA) powder shows similar behavior to PPTA before and after annealing. A block copolymer of PBA with nylon 6 (80% PBA) showed a much sharper peak for the aramid nitrogens consistent with a greater degree of uniformity and order in this material. While detailed assignment of all peaks observed is not complete, the value of the method for characterizing aramid-containing materials was clearly demonstrated.



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	<del>20</del>

**$^{15}\text{N}$  CP/MAS NMR of Aramids: A New Tool for Characterization  
of the Morphology of High Modulus Fibers for Composites**

Douglas G. Powell and Lon J. Mathias\*  
Department of Polymer Science  
University of Southern Mississippi  
Hattiesburg, Mississippi 39406-0076

**INTRODUCTION**

In recent years, high modulus aromatic polyamides have become important in the fabrication of high performance composites. Current methods of fiber manufacture involve coagulation and orienting of fibers from liquid crystalline solution prior to impregnation and cure with a suitable matrix. To achieve ultimate modulus and tensile properties, several workers have attempted to disperse these high modulus fibers at the molecular level to generate molecularly reinforced composites.<sup>1-4</sup> This dispersion has been achieved either through coagulation of the fibers in the presence of a suitable matrix<sup>1-3</sup> or by *in situ* reactions to form a matrix around solution dispersed fibers.<sup>4</sup>

Polymer crystallinity, amorphous regions, stress-induced kinking<sup>5</sup> and other non-isotropic behavior play important roles in achieving, or limiting, the ultimate strength of the composite. Unfortunately, methods for direct analysis of insoluble, intractable fibers and composites are limited.

We recently reported the utility of  $^{15}\text{N}$  CP/MAS NMR in analysis of crystalline morphology of solid polyamides as well as aramid-amide copolymers.<sup>6,7</sup> Unlike x-ray, the NMR technique was found to be sensitive to both crystalline and amorphous regions in the polymer. We report here the  $^{15}\text{N}$  NMR analysis of some commercial aramids processed under different conditions. In addition, the  $^{15}\text{N}$  NMR spectra of previously reported molecular composites are presented to demonstrate the power of this technique in readily observing changes in dispersion at the molecular level.

## EXPERIMENTAL

Samples of poly(p-benzamide) (PBT) powder and Kevlar (PPTA) pulp and fiber and were obtained from E. I. Dupont Chemical Co., Wilmington, Delaware. Molecular composites containing from 10 to 50% PPTA with 15% nylon 3 grafts in a matrix of nylon 3 were prepared as previously described.<sup>4</sup> Films of PPTA were prepared by dissolving the PPTA pulp in concentrated sulfuric acid and then casting on a glass plate. The films were coagulated by irrigating with distilled water. The films were lifted from the glass and extracted overnight with water and then dried *in vacuo* at 80°C overnight. Selected samples were annealed at 400°C under flowing nitrogen.

<sup>15</sup>N CP/MAS NMR spectra were obtained on a Bruker MSL-200 at a frequency of 20.287 MHz and <sup>1</sup>H frequency of 200.13 MHz. A standard cross polarization pulse sequence was used with a contact time of 1-2 ms. Other experimental parameters have been described previously.<sup>6</sup>

## RESULTS

Figure 1 shows the <sup>15</sup>N CP/MAS NMR spectra of PPTA prepared under various conditions. The top trace shows a sample coagulated into water from a 4% solution in H<sub>2</sub>SO<sub>4</sub>. The middle trace shows the same sample after annealing at 400 °C for 8 hours. PPTA coagulated from dilute (< 8%) H<sub>2</sub>SO<sub>4</sub> solutions has been shown to contain a large amorphous fraction which can be crystallized by annealing at elevated temperatures.<sup>8</sup> The <sup>15</sup>N NMR spectra show this change as the disappearance of outer resonances in the broad absorbance combined with an overall linewidth narrowing. The lower spectrum of the highly oriented fiber demonstrates convincingly the narrowing of linewidth as the degree of crystallinity and ordering increases.

Figure 2 shows the <sup>15</sup>N CP/MAS NMR spectra of molecular composites prepared by grafting of nylon 3 onto dispersed PPTA. The spectra show, from top to bottom, 10%, 20%, 30%, and 50% PPTA by weight in the composite. The lower trace shows a water precipitated and annealed sample of PPTA. Interestingly, the linewidth of this peak

and the 50 weight percent composite show little difference indicating the PPTA is highly crystalline in this composite. The upper traces with 10 to 30 weight percent show substantial broadening in the PPTA resonance comparable to Figure 1 (upper trace) indicating lower order in the PPTA crystal structure plus amorphous regions in the PPTA. This agrees with previous characterization of these materials by x-ray and IR which concluded that good dispersion was possible at loadings of 30% PPTA or less.<sup>4</sup> At levels above this, PPTA begins to aggregate due to the incompatibility of the PPTA with the nylon 3 matrix. <sup>15</sup>N CP/MAS NMR analysis thus provides a simple non-destructive technique for probing the dispersion and relative crystallinity of the rigid-rod reinforcement in a molecular composite.

Figure 3 compares samples of PBT homo- and block copolymers. The upper trace is of an as-obtained powder sample with an intrinsic viscosity reported to be 1.18 dL/g. Surprisingly broad peak width (or a large number of overlapping peaks) was observed which narrowed significantly on annealing (middle trace). The bottom trace is of a PBT-nylon 6 block copolymer<sup>6</sup> containing 80% aramid segments. The presence of the flexible nylon 6 units apparently allows facile crystallization of the PBT blocks leading to sharper peaks that we attribute to more uniform crystallites than observed for the PBT homopolymer.

## CONCLUSIONS

The utility of <sup>15</sup>N NMR for morphological evaluation of solid aramids and composites has been demonstrated. While chemical shift changes are small compared to those observed for nylons, the linewidth of the nitrogen resonance appears highly sensitive to the presence of amorphous regions and the degree of order and dispersion of rigid rod molecules in a composite or block copolymer. We are currently examining other aramid polymers and model compounds in an attempt to relate local morphology to <sup>15</sup>N NMR data. We conclude that <sup>15</sup>N CP/MAS NMR is a sensitive technique for

examining these materials at the molecular level with the potential for correlation with macroscopic properties.

## ACKNOWLEDGEMENTS

We wish to acknowledge the Office of Naval Research for partial support of our work in molecular composites; a Department of Defense grant for the purchase of our solid state NMR spectrometer; Dr. K. H. Gardner of DuPont for samples; and Dr. D. R. Moore for preparation and characterization of the nylon 3 composites.

## REFERENCES

1. Takayanagi, M.; Ogata, T.; Morikawa, M.; Kai T. *J. Macromol. Sci. Phys.*, **1980**, B17(4), 591.
2. Takayanagi, M.; *Pure Appl. Chem.*, **1983**, 55, 819.
3. Kumumaru, F.; Oono, T.; Kajiyama, T.; Takayanagi, M. *Polym. Compos.*, **1983**, 4, 135.
4. Moore, D. R.; Mathias, L. J. *J. Appl. Polym. Sci.*, **1986**, 32, 6299.
5. Martinez, G.; Piggott, M.; Bainbridge, D.; Harris, B. *J. Mat. Sci.*, **1981**, 16, 2831.
6. Powell, D.; Sikes, A.; Mathias, L. *Macromolecules*, **1988**, 21, 1533.
7. Mathias, L.; Powell, D.; Sikes, A. *Polym. Commun.*, in press.
8. Chatzi, E.; Koenig, J. *Polym.-Plast. Technol. Eng.*, **1987**, 26, 229.

## LIST OF FIGURES

- Figure 1.**  $^{15}\text{N}$  CP/MAS spectra of water coagulated PPTA (upper trace); precipitated PPTA annealed at 400°C for 8 hours (middle trace); and commercial PPTA oriented fiber (lower trace).
- Figure 2.**  $^{15}\text{N}$  CP/MAS spectra of PPTA/nylon 3 molecular composites (top to bottom): 10%; 20%; 30%; 50% PPTA; and annealed PPTA precipitate shown for comparison.
- Figure 3.**  $^{15}\text{N}$  CP/MAS spectra of PBT as-obtained powder (upper trace); annealed powder (middle); and 80% PBT-nylon 6 block copolymer (lower trace).







